The influence of oil on the properties of slowly-cooled jet-cooked normal corn starch dispersions

Jeffrey A. Byars\textsuperscript{a,*}, George F. Fanta\textsuperscript{a,b}, Frederick C. Felker\textsuperscript{a,b}

\textsuperscript{a}Cereal Products and Food Science, United States Department of Agriculture, National Center for Agricultural Utilization Research, Agricultural Research Service, 1815 N University Street, Peoria, IL 61604, USA
\textsuperscript{b}Plant Polymer Research Units, United States Department of Agriculture, National Center for Agricultural Utilization Research, Agricultural Research Service, 1815 N University Street, Peoria, IL 61604, USA

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Abstract

Previous work has shown that when aqueous dispersions of normal corn starch are jet-cooked under excess steam conditions, the properties of the final product depend on the manner in which the cooked dispersion is cooled. Phase separation of the component molecules of starch alters the final properties, and the extent of phase separation depends on the cooling conditions. Both irregular, amorphous particles and spherical or toroidal crystalline particles were observed in the cooled products. Stable starch-oil composites with a wide range of applications are formed if oil is jet cooked with starch, and the goal of this work was to examine the effect of the added oil on the rheological and structural properties of cooled dispersions. A Rapid Visco Analyser was used to obtain a range of cooling profiles and stirring rates. The dynamic moduli increased with the addition of oil, and the effect was greater for mineral oil than soybean oil. Light microscopy showed that the crystalline particles were not formed in the presence of oil, but samples with oil contained different types of large and small spherical particles. The change in behavior is attributed to the selective extraction of fatty acid components of native lipid by the oil droplets, or to the preferential accumulation of amylose–lipid helical inclusion complexes at the oil droplet surface.

Keywords: Steam jet cooking; Starch–oil composite; Complex formation; Phase contrast microscopy; Rheology

I. Introduction

Steam jet cooking is a rapid and continuous process for preparing starch dispersions for industrial applications, for example, in the paper industry (Klem & Brogly, 1981). The high-temperature and high-shear conditions of excess steam jet cooking completely dissolve granular starch and reduce its molecular weight (Byars, 2003; Dintzis & Fanta, 1996). When an oil or lipophilic material is jet-cooked with the starch, the resulting material is a stable starch–lipid composite in which the micrometer-size lipid droplets do not separate or coalesce (Eskins & Fanta, 1999). As part of a continuing research program on starch utilization, we are studying the properties and applications of these starch–lipid composites. The stability of the lipid droplets with respect to coalescence has been shown to be caused by the accumulation of starch at the lipid–water interface (Fanta, Felker, Eskins, & Baker, 1999).

We have also studied the properties of jet-cooked starch dispersions in the absence of oil. When a jet-cooked starch sample cools slowly, particles can form due to crystallization of helical inclusion complexes of amylose with the native lipids present in the starch granule (Davies, Miller, & Proctor, 1980; Fanta, Shogren & Salch, 1999). Fanta, Felker, and Shogren (2002) showed that both small (5–15 \textmu m diameter) toroidal particles and larger, more spherical particles (20–60 \textmu m diameter) can be formed from starch dispersions containing both amylose and native lipids.

The conditions under which a jet-cooked starch dispersion is cooled have also been shown to affect
the rheological properties of cooked dispersions (Byars, Fanta, & Felker, 2003). At starch concentrations above 5 wt%, the amyllose and amylopectin components of starch form separate phases, and a dispersion that is slowly cooled without stirring is a low viscosity liquid. If the same sample is stirred while cooling, the amyllose and amylopectin interact to form a gel network, and the cooled product is a weak gel with a higher viscosity. At low starch concentrations, phase separation does not occur, and a strong gel is formed whether or not the sample is stirred during cooling. In all cases, both toroidal and spherical crystalline particles are formed. This study extends on this earlier work by considering the effect of added oil on the properties of slowly-cooked, jet-cooked starch dispersions. Microscopy and rheological measurements are used to examine the microstructure and physical properties of the starch-oil composites.

2. Materials and methods

2.1. Jet cooking

Normal corn starch (pure food-grade corn starch from A. E. Staley, Decatur, IL, USA) was suspended in distilled water using a Waring (East Windsor, NJ, USA) blender. The initial concentration of granular starch was varied from 7.0 to 14.1 wt% on an as is basis. Mineral oil or soybean oil was added on a weight basis relative to the starch. Samples are designated as the weight percent starch and the ratio of starch to oil by weight. This slurry was passed through a jet cooker under excess steam conditions, and the cooked product was collected and analyzed. The slurry was delivered to the jet cooker by a Moyno progressing cavity pump (Robbins Meyers, Springfield, OH, USA) at a flowrate of about 1 L/min. The starch slurry and steam were combined in a Penick and Ford hydroheater (Penford Corp, Cedar Rapids, IA, USA). Steam was supplied at 550 kPa (65 psig), and the backpressure in the hydroheater was set at 380 kPa (40 psig). The inlet steam pressure was lower than in our previous work (70 psig) due to plumbing changes external to the jet cooker. The lower steam pressure was used to maintain the same conditions within the jet cooker. The cooked product was collected in a preheated Dewar flask. Percent starch solids in the jet cooked dispersions was determined by freeze drying accurately weighed portions of each cooked dispersion. Determinations were carried out in replicate, and the results were averaged. The standard deviation of the solids concentration of the cooked dispersions was less than 0.2 wt% for each initial concentration. The reported concentrations are lower than the starting concentrations due to dilution during cooking.

For the experiments with defatted starch, samples were defatted by heating a stirred suspension of 175 g starch in 5 vol% methanol (1700 mL methanol plus 300 mL water) under reflux for 2 h (Morrison & Coventry, 1985). Starch was separated by filtration, and a second extraction was carried out under identical conditions. Two additional extractions were then carried out under the same conditions with refluxing 75 vol% n-propanol/water (1500 mL n-propanol plus 500 mL water). The extracted starch was allowed to air dry and was further dried under vacuum at 55 °C.

2.2. Cooling conditions

A Rapid Visco Analyser (RVA) (Newport Scientific, Warriewood, NSW, Australia) was used to control the cooling rate and stirring conditions of the sample. Cooked starch (30 mL) was placed in a sample cup preheated in boiling water and transferred to the RVA. All cooling profiles began with two minutes stirring at 360 rpm at 95 °C to eliminate any effects of sample handling and cooling during transport between the jet cooker and the RVA. Samples were cooled from 95 to 25 °C over a 4-h period (~0.3 °C/min), with either stirring at 60 rpm or no stirring. In order to prevent drying of the sample during cooling, the top of the sample cup was sealed with an o-ring. The torque measured by the RVA therefore did not provide information about the viscosity of the sample during cooling.

2.3. Microscopy

Approximately, 1 mL of sample was removed from the RVA cup and stored overnight at room temperature. Storage time did not affect the structure of samples as observed by microscopy. A drop of sample (30 μL) was placed on a glass slide, and a coverslip was applied and allowed to settle while the drop spread under the weight of the coverslip. After several minutes, the motion of the sample subsided and a stationary field was selected from near the middle of the sample to avoid areas subject to differential migration of particles. Samples were observed with a Zeiss Axioskop light microscope (Carl Zeiss, Inc., Thornwood, NY, USA) using phase contrast optics, and representative fields were photographed using a Kodak DCS 460 digital camera (Eastman Kodak Co., Rochester, NY, USA). Phase contrast microscopy was chosen to examine microstructure to avoid artifacts due to dilution, staining or sample preparation. The fields shown were chosen to display best the kinds of particles and domains contained in the sample, not necessarily reflecting their relative abundance.

2.4. Rheology

Measurements in steady shear flow and small amplitude oscillatory shear flow were conducted on a TA Instruments (New Castle, DE) ARES controlled strain fluids rheometer. Tests were performed with a 50 mm diameter cone-and-plate geometry. Small amplitude oscillatory shear measurements were conducted at a strain of 1%, which was within the linear viscoelastic region for all samples. No thixotropy
was observed in measurements of the viscosity. A circulating water bath was used to maintain the temperature at $25.0 \pm 0.1 \, ^\circ C$, and humidity covers were used to prevent drying of the samples. All measurements were performed in duplicate, and average values are reported. The results presented are for cooled samples that have attained steady values of their rheological properties. The standard deviations between repeated measurements for a given cooked dispersion, as well as between the average values of measurements from multiple cooks cooled under the same conditions, were less than 10%.

3. Results

Fig. 1 shows light micrographs of samples with starch contents of 10 wt% that were stirred while being cooled. The sample shown in Fig. 1a contained starch and mineral oil (100:20, by weight), whereas the sample in Fig. 1b contained only normal corn starch. Both samples consist primarily of a gel network of rough, amorphous particles and an aqueous continuous phase that appears as a grey background. The oil appears in Fig. 1a as 1–10 $\mu m$ droplets (labeled with arrows). Fanta et al. (1999) showed that the oil droplets are covered by a thin starch film that prevents their coalescence. In the absence of oil, large ($\sim 20–30 \, \mu m$ diameter) spherical crystallites (labeled s) and smaller ($\sim 5 \, \mu m$ diameter) toroidal crystallites (labeled t) are present. Fanta et al. (2002) used birefringence and X-ray diffraction to establish the crystallinity of these particles. The powder diffraction patterns of the particles showed that the particles were formed by the crystallization of helical inclusion complexes of amylose and the small amount of native lipid normally present in corn starch. The absence of the crystallites in the sample containing oil suggests that these helical inclusion complexes are no longer available for crystallite formation.

The effect of the oil droplets on the rheology of the cooled dispersions is shown in Fig. 2. The viscosity (Fig. 2a) is shown for the samples of Fig. 1 with mineral oil, as well as for a sample containing soybean oil. Both samples with oil have higher viscosities than the sample with only starch, especially at lower shear rates, where the sample behaves like a gel. At high shear rates, the gel structure of the sample is broken down, and all of the samples have similar viscosities. A small increase in the viscosity is expected due to the added oil, but this effect does not account for the large changes shown in Fig. 2a. For a suspension of non-

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![Fig. 1. Phase contrast micrograph of a 10 wt% normal corn starch dispersion cooled in 4 h with stirring (a) with mineral oil at a starch:oil level of 100:20 and (b) without oil (a, amorphous gel network; s, spherical crystallite; t, toroidal crystallite).](image1)

![Fig. 2. (a) Viscosity and (b) linear viscoelastic properties of 10 wt% normal corn starch dispersions cooled in 4 h with stirring. The solid symbols show the storage modulus and the open symbols show the loss modulus for each composition.](image2)
interacting hard spheres with volume fraction \( \phi \) in a Newtonian solvent with viscosity \( \eta_s \), the viscosity is expected to be \( \eta = \eta_s (1 + 2.5\phi) \) (Macosko, 1994). In this case, \( \phi \approx 0.02 \), so the viscosity is expected to increase by 5% due to the presence of the oil droplets. Instead, the viscosity at \( \gamma = 10^{-3} \) s\(^{-1}\) is 140% greater for the sample with mineral oil, and 50% greater for the sample with soybean oil.

The storage modulus, \( G' \), and the loss modulus, \( G'' \), for the same samples are shown as functions of frequency, \( \omega \), in Fig. 2b. As expected from the viscosity measurements, the linear viscoelastic properties are also greater for the oil-containing samples. The larger differences at low frequency are further indications of stronger long-range gel interactions, while the similarity at high frequency indicates that on shorter length scales the samples remain similar. Byars et al. (2003) showed that samples at high (\( > 5 \) wt\%) starch concentrations without oil were characterized as weak gels, with the storage modulus of a similar magnitude to the loss modulus over the entire frequency range. The samples with oil examined in the present study all showed the same qualitative behavior of being weak gels, but addition of oil resulted in the formation of slightly stronger gels, as indicated by the larger increase in \( G' \) than in \( G'' \). One measure of the strength of a gel is given by the ratio \( \tan \delta = G''/G' \), with a lower value indicating a stronger gel. For the samples in this study, at \( \omega = 1 \) rad/s, \( \tan \delta = 1.8 \) for the sample without oil, 1.6 for the sample with soybean oil, and 1.2 for the sample with mineral oil.

If a jet-cooked dispersion at high starch concentration with no added oil is not stirred while cooling, the amorphous gel network shown in Fig. 1a does not form, and the value of the storage modulus is lower than for the stirred sample (Byars et al., 2003). The same behavior is observed in the presence of oil, as shown in Fig. 3. Neither the amorphous gel nor the crystalline particles are observed for the unstirred sample, but a previously unobserved type of particle is present in the sample shown in Fig. 3a (particles indicated by arrows). Powder X-ray diffraction and the birefringence patterns observed through cross-polarizing filters suggested that these particles might contain small crystalline regions in a matrix of amorphous retrograded starch. A complete description of the properties of these aggregates and other particles formed from slowly-cooled dispersions of jet-cooked starch and oil is presented in another manuscript (Fanta, Felker, Shogren, Byars, & Salch, in press). Fig. 3b shows that the same trends were observed in the rheological properties as for the stirred samples. The storage modulus increases at low frequency for samples containing oil, and the effect is greater for mineral oil. The storage modulus is much lower than for the stirred samples shown above, and the gel strength decreased. For these samples, \( \tan \delta \) at a frequency of 1 rad/s was 4.1 for the sample without oil, 2.8 for the sample with soybean oil and 1.8 for the sample with mineral oil.

The effect of the concentration of oil droplets on the rheological properties is shown in Fig. 4. At a starch:oil ratio of 100:10, there was no significant difference in the rheological properties relative to the sample without oil, although the crystalline particles were not observed at this concentration.
oil level. At higher oil levels of 100:20 and 100:40, the storage modulus increased with increasing oil levels, and for an oil level of 100:40, \( \tan \delta \) at a frequency of 1 rad/s was 0.9.

The effect of oil levels lower than 100:10 on the structure of the sample is shown in Fig. 5 for stirred 10 wt% starch dispersions with mineral oil in the ratio 100:5 (Fig. 5a) and 100:2 (Fig. 5b). As observed with 100:10 oil, an oil level of 100:5 also prevented the formation of crystalline particles. At the oil level of 100:2, however, the same large crystalline particles were formed as in the absence of oil. The rheological measurements for both of these samples were the same as for the no oil and 100:10 oil level samples in Fig. 4 (results not shown). Although quantitative data on the droplet size distribution are not available, the droplets in Fig. 5 appear smaller than those at the oil level of 100:20 in Fig. 1.

Experiments with 7.5 and 6.25 wt% starch followed the same trends as the results above for 10 wt% starch. In all cases, the addition of oil increased the storage modulus relative to a sample without oil. Mineral oil typically led to about twice as large an increase as for soybean oil, and there was a greater increase for samples that were not stirred during cooling. The spherical aggregates of Fig. 3a were observed for unstirred samples prepared in the presence of oil, and the crystalline particles shown in Figs. 1b and 5a were not observed for any sample with oil at a level of 100:10 or greater.

Fig. 6a shows a micrograph of a sample at 5 wt% with mineral oil at a 100:20 level that was not stirred during cooling. As observed for samples without oil (Byars et al., 2003), the gel formed under these conditions had a smoother texture than gels formed at higher concentration. Also, the presence of oil in this sample prevented crystallites from being formed. Fig. 6b shows the storage and loss moduli for this sample, as well as for a sample containing soybean oil, a sample with no oil, and a sample prepared from defatted starch. The rheological properties of each sample are characteristic of a strong gel, with \( G' > G'' \) over the entire frequency range and with a much weaker frequency dependence than for the weak gels. The relative increase in rheological properties for samples with oil was about the same at 5 wt% as at the higher starch concentrations. The storage modulus for the sample with defatted starch is about twice as high as for the sample with mineral oil.

### 4. Discussion and conclusions

In our previous study carried out on corn starch jet cooked in the absence of oil (Byars et al., 2003), we proposed that phase separation takes place to yield aqueous phases rich in either amylose or amylopectin (Kalichevsky et
Since amylopectin is the major component of normal dent corn starch, the continuous phase should consist largely of amylopectin, with aqueous amylose droplets forming the dispersed phase. In the absence of stirring, retrogradation and gel formation of amylose is expected to occur largely within the separated aqueous amylose droplets and have little effect upon the rheology of the continuous amylopectin phase. Viscosity build-up and gel formation in the amylopectin phase would thus be minimal over the time frame of these experiments. The previous results suggest that stirring these jet-cooked dispersions during cooling may inhibit this phase separation. The concentration of amylose in the continuous phase would be higher, relative to unstirred experiments, producing the higher viscosities and storage moduli that are observed when dispersions are stirred. Stirring may also promote interaction and hydrogen bonding between amylose and amylopectin, thus accounting for the gel network observed in stirred dispersions. A stronger gel was observed when a 10.2 wt% starch dispersion was cooled with stirring over a 1-h period, rather than 4 h, suggesting that with more rapid cooling, retrogradation and gelling of amylose takes place before phase separation of aqueous amylose and amylopectin can occur.

Formation of amylose/native lipid inclusion complexes will also affect the rheology of jet-cooked starch dispersions, since these complexes interfere with and retard the normal processes of starch retrogradation and gel formation. We have observed this effect previously in cooled dispersions of corn starch/paraffin wax prepared by steam jet cooking (Fanta, Felker, Shogren, & Knutson, 2001). Whereas a firm gel was obtained when defatted starch was used, the dispersion did not gel when native lipid was still present. We also observed (Byars et al., 2003) that modulus values for corn starch, jet cooked at 5.2 wt% and cooled over a 4-h period, were higher when starch was defatted.

Although the complex modulus steadily declined as starch concentrations were reduced from 10.2 to 6.6 wt%, a sharp increase was observed at 5.2 wt%, coupled with a decrease in the loss tangent (Byars et al., 2003). These results were not surprising, since a lower rate of amylose/amylpectin phase separation would be expected at the lower starch concentration of 5.2 wt%, and this could result in retrogradation and gelling of amylose before phase separation can occur. Stirring during cooling would not be expected to increase the modulus and viscosity of the 5.2 wt% dispersion, because the slow rate of phase separation at this concentration should be minimally affected by stirring. In agreement with this supposition, the complex modulus of the stirred sample at 5.2 wt% was actually lower than that observed without stirring, probably because stirring can promote interaction between amylose and amylopectin and thus interfere with the normal retrogradation and gelling of amylose. For the samples at high starch concentrations for which amylose/amylopectin phase separation is favored, the viscous properties (i.e. loss modulus) will increase with increasing starch concentration, thereby increasing the value of the complex modulus.

Formation of water-insoluble crystallites from amylose/native lipid complexes (Fanta et al., 2002) can also take place in these jet-cooked dispersions, and crystallite formation can affect the rheological properties by removing both lipid and a portion of the dissolved amylose from solution. In the absence of added oil, these crystallites are observed both with and without stirring; however, the effect of stirring upon crystallite yield and morphology has not yet been determined. Crystallites were not formed when the cooling period was reduced to 1 h, consistent with the results of Davies et al. (1980), who found that an extended storage time above 75 °C was required for crystallite formation.

Whereas crystallites were formed in corn starch dispersions jet cooked without oil, these crystalline particles were absent when dispersions were prepared from 10 wt% corn starch and 100:20, 100:10 and 100:5 starch:mineral oil, and the dispersions were cooled over a 4-h period with stirring. When the amount of mineral oil was reduced to 100:2, spherical crystallites were once again observed. Gel networks of rough, amorphous particles were observed both with and without oil.

Rheological properties of 10 wt% corn starch, cooked with 100:10, 100:5 and 100:2 mineral oil, were about the same as those observed in the absence of oil; however, samples prepared with 100:20 and 100:40 oil had higher viscosities and a higher storage moduli, both with and without stirring, than samples prepared without oil. A mineral oil level of 100:40 produced the highest storage modulus with 10 wt% starch. As observed in the absence of oil, stirring during the 4 h cooling period increased both the viscosity and storage modulus. Viscosities and storage moduli were higher with mineral oil than with soybean oil. Results with starch concentrations of 7.5 and 6.25 wt% followed the same general trends as experiments carried out at a concentration of 10 wt%. As observed for the series of samples jet cooked without oil, the storage modulus of the 5.2 wt% sample jet cooked with 100:20 oil was higher than that of a comparable sample prepared at 10 wt% concentration, and the rheological properties were characteristic of a strong gel. The reasoning presented above to explain the sharp increase in modulus at 5.2 wt% starch with no oil can also be used to explain the behavior of these oil-containing dispersions. At this starch concentration and a mineral oil concentration of 100:20, the storage modulus was about twice as high when defatted starch was used. Perhaps, the best explanation for the observed effects of dispersed oil droplets on the microstructure and rheological properties of these jet cooked dispersions is the ability of the oil droplets to remove native lipid (particularly free fatty acids) from jet-cooked dispersions. Oil droplets can remove lipid by dissolving and extracting it from cooked aqueous dispersions before the formation of amylose complexes can take place. The dispersed
micrometer-sized oil droplets can also provide a large surface area for adsorption of either uncomplexed or complexed (with amylose) lipid material. The fact that crystallites usually observed with corn starch in the absence of oil do not form in these oil-containing dispersions is consistent with this theory. The higher storage modulus observed with mineral oil, as compared with soybean oil, might occur because mineral oil is a better solvent for native lipid. Mineral oil might also provide a more hydrophobic surface for lipid adsorption. Reasons given earlier to explain the effects of stirring on rheology in the absence of oil should still apply when oil droplets are present. Stronger gels may be formed in jet cooked dispersions prepared with oil because more of the native lipid has been removed from the system. This would allow more amylose to remain in solution since there would be less lipid present to complex with amylose and interfere with the retrogradation and gelling process. It appears that not all the lipid has been removed, however, since use of defatted starch produced a cooked dispersion with a higher storage modulus than starch that contained native lipid.

A previously unobserved type of spherical particle was observed when a 10 wt% starch, 100:20 mineral oil sample was cooled over a 4-h period without stirring. These particles were observed at corn starch concentrations of 7.5 and 6.25 wt%; however, no particles were observed at 5.2 wt%. Formation of these particles may be explained if fatty acids, which comprise most of the native lipid material present in commercial corn starch, are selectively dissolved or adsorbed by oil droplets, due to their greater hydrophobicity, relative to the lysophospholipids. Amylose could then complex with the remaining lysophospholipids to form the particles observed. Consistent with this idea are the observations that (1) lysophospholipids are the major components of the native lipid present in wheat starch (Morrison, 1988); and (2) the particles formed from corn starch in the presence of oil are similar in appearance to particles isolated from slowly-cooled, jet cooked wheat starch dispersions prepared in the absence of oil. Additional experiments on the formation and characterization of starch/native lipid crystallites prepared in the presence and absence of oil will be reported in a separate publication.

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References


